H/Allyl and Alkyl/Allyl Conical Intersections: Ubiquitous Control Elements in Photochemical Sigmatropic Shifts

Sarah Wilsey† and K. N. Houk*,§

Physical and Theoretical Chemistry Laboratory
University of Oxford, South Parks Road
Oxford OX1 3QZ, UK
Department of Chemistry and Biochemistry
University of California
Los Angeles, California, 90095-1569

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The complexity of alkene photochemistry has exasperated attempts at a simple theoretical description.[1] We have discovered a feature of excited-state potential surfaces which is common to a wide variety of alkenes. A new type of conical intersection, the "H/allyl CI", has a remarkably constant structure for many alkenes and is closely related to its more familiar counterpart, the "alkyl/allyl CI".[2,3] These conical intersections are the gateways between $\pi\pi^*$ excited singlet states and ground-state potential surfaces and hold the key to understanding much of the photochemistry of alkenes.

Conical intersections play a fundamental role in organic photochemistry, giving rise to ultrafast decay processes in many different systems.[4] In polyatomic molecules, two states of the same symmetry and multiplicity will intersect along an $(n - 2)$-dimensional hyperline, where n is the number of degrees of freedom in the molecule. The other two coordinates, $\mathbf{x_1}$ and $\mathbf{x_2}$, which are related to the gradient difference and nonadiabatic coupling vectors, define a branching space; only nuclear distortion in this plane lifts the degeneracy. The name "conical intersection" is derived from the characteristic double cone topology obtained when the energy is plotted in this branching space (Figure 1); the detailed shapes of these surfaces are often much more complex than indicated by this cartoon.[4−6] Methods have now been developed[5] which enable the location of the lowest energy point on these conical intersection hyperlines, and these have been found for a wide variety of organic photochemical reactions. The conical intersection is expected to result in efficient internal conversion to the ground-state surface, normally within a vibrational period of a molecule.

Simple nonconjugated alkenes possess Rydberg (π−3s) and valence $^1(\pi\pi^*)$ states that lie very close in energy.[1] The Rydberg (π−3s) state is generally thought to give rise to carbene products, although a conical intersection corresponding to a H-transfer from one of the zwitterionic states in ethene leading to carbene has also been reported.[6] The $^1(\pi\pi^*)$ state gives predominantly $E-Z$ isomerization via an avoided crossing, but can also lead to carbon and hydrogen sigmatropic shifts.[1] While conical intersections have already been located for carbon sigmatropic shifts,[2,3] we report for the first time the existence of analogous structures for hydrogen sigmatropic shifts.

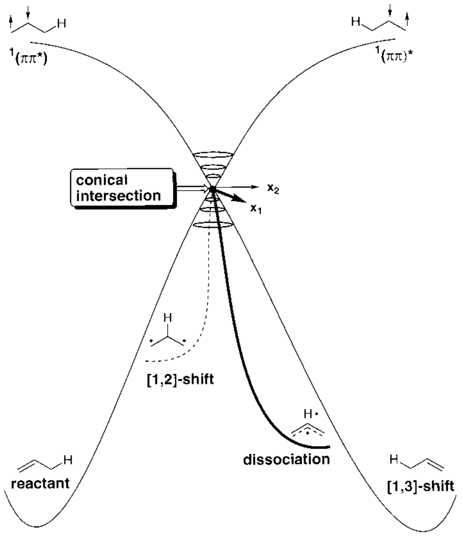

Figure 1. Diagram showing the relationship between the excited state, H/allyl conical intersection and the ground-state products of propene. The gradient difference vector, $\mathbf{x_1}$, corresponds to a motion leading to the trimethylene diradical ([1,2]-shift) or to dissociated radicals, while the nonadiabatic coupling vector, $\mathbf{x_2}$, corresponds to the formation of reactant or isomeric [1,3]-shift product.

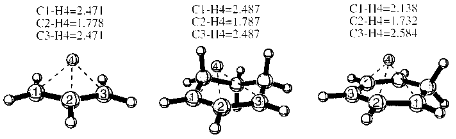

Figure 2. CASSCF/6-31G* optimized geometries of the lowest energy points of the H/allyl conical intersections in propene (**1**), cyclohexene (**2**), and 1,4-cyclohexadiene (**3**).

We employed the CASSCF method with appropriate active spaces, the 6-31G* basis set and the conical intersection algorithm[5b] implemented in GAUSSIAN 94.[7] We have located H/allyl conical intersections for propene (**1**), cyclohexene (**2**) and 1,4-cyclohexadiene (**3**), shown in Figure 2. Each consists of a nearly planar allyl radical with a hydrogen atom interacting with the central carbon. The H−C1, H−C2, and H−C3 distances are 2.5, 1.8, and 2.5 Å, respectively, in the prototypical propene system. Similar bond lengths are found in the other systems, although **3** is substantially distorted from the regular tetrahedral geometry due to conjugation with the additional double bond. In each case there are four quasi-unpaired electrons that can recouple in four different ways leading to reactant, a trimethylene diradical (via a [1,2]-shift), isomeric [1,3]-shift product or dissociated radicals. Gradient difference and nonadiabatic coupling vectors characterize the directions in which the excited-state and ground-state degeneracy is broken. A simple schematic representation of the relationships between the excited state, the conical intersection,

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[†] University of Oxford.

[§] University of California.

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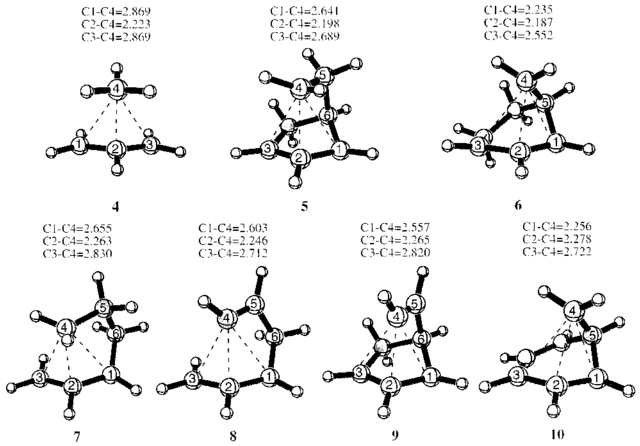

Figure 3. CASSCF optimized geometries of the lowest energy points of the alkyl/allyl conical intersections for but-1-ene (**4**),[6] norbornene involving cleavage of the ethano bridge (**5**) and cleavage of the methano bridge (**6**),[2] cyclohexene (**7**), 1,4-cyclohexadiene (**8**), norbornadiene involving cleavage of the vinylic bridge (**9**) and cleavage of the methano bridge (**10**).

and the various species that can be formed on the ground-state surface of propene is shown in Figure 1. The gradient difference vector, $\mathbf{x_1}$, corresponds to a C2−H stretch which leads to either a trimethylene diradical or to H plus allyl radicals. The nonadiabatic coupling vector, $\mathbf{x_2}$, corresponds to a C1−C2−C3 asymmetric stretch leading to formation of either a C1−C2 or a C2−C3 double bond; recoupling of the single electron on the H radical with the remaining unpaired electron on the allyl fragment would then lead back to the reactant or to the isomeric [1,3]-shift product.

Bernardi, Olivucci, Robb, and Tonachini earlier identified a tetrahedral alkyl/allyl conical intersection (**4**) for but-1-ene, shown in Figure 3.[8] Similar structures were located in other alkene systems: the excited-state singlet di-π-methane rearrangement of 1,4-pentadiene,[9] the oxadi-π-methane rearrangement of but-3-enal[10] and the [1,2]- and [1,3]-allyl-shifts in 1,5-hexadiene[11] all involve similar conical intersection structures which we would call vinyl/allyl, acyl/allyl, and allyl/allyl CIs. We also reported alkyl/allyl polycyclic conical intersections in our investigation of the ground- and excited-state surfaces of norbornene.[2] The $^1(\pi\pi^*)$ state of norbornene undergoes efficient cleavage of either the methano or ethano bridges, leading to two distinct conical intersections (**5** and **6** in Figure 3). For all of these conical intersections, there are four different ground-state pathways that can be accessed after decay: return to reactant, [1,3]-shift, diradical formation by [1,2]-shift, or bond cleavage. Cyclopropanes can be formed from the trimethylenes, and vibrationally excited retro-Diels−Alder products can be formed from the diradical resulting from bond cleavage in norbornene.

We have now located the alkyl/allyl conical intersections (Figure 3) formed from $^1(\pi\pi^*)$ cyclohexene (**7**), 1,4-cyclohexadiene (**8**) and norbornadiene (**9** and **10**). Two possible C−C bond cleavages (corresponding to bond breaking to the vinylic or methano bridges) are possible in norbornadiene leading to decay through structures **9** and **10**, respectively. In each case the C3−C4 bond is broken, and C4 moves over the plane of the C1−C2−C3 moiety, giving rise to the characteristic tetrahedral structure. As with the H/allyl CIs, the C1−C2−C3 atoms form a planar allylic fragment, while the fourth carbon lies above the plane and 2.2−2.3 Å away from C2 (compared to 1.8 Å in the H/allyl structures). This C−C bond length is similar to the partial bond lengths found in pericyclic reaction transition states.[12] The distances from the bridging carbon to the allyl termini are 2.6−2.9 Å, except for **6** and **10**, where a homoallylic carbon is held only 2.2−2.3 Å from one allyl terminus. Such a structure was also located by Robb et al. as a key topological feature in the excited-state photocycloaddition of ethene to benzene.[3]

Table 1. CASSCF/6-31G* Energies (kcal/mol) of the H/Allyl and Alkyl/Allyl Conical Intersections, Dissociated Radicals and Vertical Excited States Relative to the Ground States of Propene (P), Cyclohexene (CH), 1,4-Cyclohexadiene (CHD), Norbornadiene (NBD), and Norbornene (NB)[a]

species	P	CH	CHD	NBD	NB
reactants	0.0	0.0	0.0	0.0	0.0
H/allyl CI	119.6	116.5	108.3		
alkyl/allyl CI		117.6	124.4	100.0[b]	104.7[d]
				87.6[c]	113.1[c]
dissociated radicals	83.8	81.5	74.8		
vertical excitation	234.4	225.8	206.2	186.4	205.5
		224.7	207.7	182.5	205.7

[a] Active spaces of (4,4)−(8,8) were used which included π and π^* orbitals, and two allylic C−C bonds or one allylic C−H bond, except for norbornene where the σ orbitals in the double bond were also included. Vertical excitation energies are given in each active space used. [b] Reaction involving initial cleavage of the vinylic bridge. [c] Reaction involving initial cleavage of the methano bridge. [d] Reaction involving initial cleavage of the ethano bridge.

Table 1 compares the energies of the H/allyl and alkyl/allyl conical intersection structures, along with the vertical excitation energies of the $^1(\pi\pi^*)$ states of propene, cyclohexene, 1,4-cyclohexadiene, norbornadiene, and norbornene. In each case the CASSCF computed vertical excitation energy for the $^1(\pi\pi^*)$ state is 8−10 eV (180−230 kcal/mol),[13] while the conical intersection lies some 80−125 kcal/mol above the ground-state reactant. For comparison, the energies of the dissociated radicals from propene, cyclohexene, and cyclohexadiene are given. In all three systems the H/allyl CI lies about 30−35 kcal/mol above the dissociated radicals. For cyclohexene, the H/allyl and alkyl/allyl conical intersections have approximately the same energy, while for cyclohexadiene, the H/allyl conical intersection lies 16 kcal/mol lower in energy than the alkyl/allyl structure. In the gas-phase experiments of the Zewail group, H-elimination is observed on photolysis of 1,4-cyclohexadiene, while cyclohexene gives rise to retro-Diels−Alder products.[14,15]

With the location of the H/allyl CI, we now have a more complete picture of the $^1(\pi\pi^*)$ photochemistry of alkenes. While $E-Z$ isomerization is believed to occur via a real avoided crossing, [1,2]-hydrogen shifts leading to carbenes, carbon and hydrogen sigmatropic rearrangements, and H-eliminations all involve conical intersections which will give rise to fully efficient decay to the ground-state surface. In many cases, several of these conical intersections will exist in the same system; the dominant pathway will depend on structural constraints in the reactant alkene that will govern how easily an excited state can evolve to each of these crossing points.

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